CCXVIII.—*The Mathematics of the Dicyclic Colour Theory, and a New Theory of the Structure of the Nitrogen Atom.*

By JAMES MOIR.

LAST year the author put forward the conception that the cause of colour in a "dicyclic" substance is the performance of an oval orbit by an electron going round the whole molecule (T., 1921, **119**, 1657). The time of revolution of the electron was taken to be identical with the time required for light to travel over a length equal to the absorption wave-length of the coloured substance.

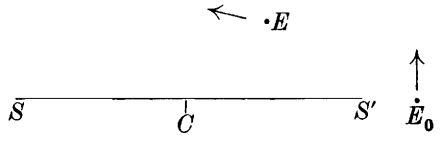
Professor W. N. Roseveare of Pietermaritzburg now supplies the following mathematical investigation of the problem, whereby it is shown, using the ordinary laws of dynamics, that an electron attracted by two equal positive nuclei *can* describe a certain elliptic orbit having its foci at the nuclei. The electron must cross the line of foci at right angles and with a velocity which is prescribed in terms of its distance, s, at that moment from the nuclei.

Professor Roseveare also obtains a formula for calculating the periodic time of revolution in the orbit in terms of the focal (inter-

focal) distance and the eccentricity of the ellipse, from which important deductions concerning the direction of the valencies of the carbon, nitrogen, and oxygen atoms are made by using the data of the colour observations.

Mathematical Investigation.

Let S and S' be the centres of force and C the middle of the line joining them. Let the electron have crossed this line at right angles outside S' at E_0 with velocity u.



Let $CE_0 = a$ and $CS = c$.

The equation of tangential motion is :

$$V\frac{dV}{ds} = -\frac{\mu}{r^2}\frac{dr}{ds} - \frac{\mu}{r'^2}\frac{dr'}{ds}.$$

This on integration gives :

$$V^2 = 2\mu\left(\frac{1}{r} + \frac{1}{r'} - K\right).$$

If the path is an ellipse with foci SS', $r + r' = 2a$ and $rr' = b'^2$, b' being the radius conjugate to CE. Then

$$V^2/2\mu = \frac{2a}{b'^2} - K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

From the preliminary conditions we find

$$K = \frac{2a}{b^2} - \frac{u^2}{2\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

Hence the path of the electron can be an ellipse with S and S' as foci provided that the equation of normal motion be satisfied, namely,

$$\frac{V^2}{\rho} = \frac{\mu}{r^2}\cdot\frac{p}{r} + \frac{\mu}{r'^2}\cdot\frac{p'}{r'},$$

wherein $$\frac{p}{r} = \frac{p'}{r'} = \frac{b}{b'}, \text{ and } \rho = b'^3/ab.$$

Thus $$\frac{abV^2}{b'^3} = \mu\frac{b}{b'}\left(\frac{1}{r^2} + \frac{1}{r'^2}\right) = \mu\frac{b}{b'^5}(4a^2 - 2b'^2),$$

whence $$V^2/2\mu = \frac{2a}{b'^2} - \frac{1}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

Hence, comparing (i) and (iii), we have $K = 1/a$, whence from (ii) we have

$$\frac{u^2}{2\mu} = \frac{2a}{b^2} - \frac{1}{a} = \frac{1}{a}\,\frac{1+e^2}{1-e^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

This equation gives the eccentricity of the ellipse in terms of the initial velocity and the distance of the electron from the mid-point of the positive forces. The latter, a, is probably practically constant, since the electron must pass close to the auxochrome groups, and the eccentricity is also consequently high, and probably constant—according to the quantum theory necessarily confined to a set of constant values, all probably high.

The time of revolution is calculated as follows:

Equation (iii) for the velocity at any point is rewritten with the substitutions $x = a\cos\phi$ and $y = b\sin\phi$, V being $\frac{ds}{dt}$.

Then
$$(a^2\sin^2\phi + b^2\cos^2\phi)\left(\frac{d\phi}{dt}\right)^2 = \frac{2\mu}{a}\left(\frac{2a^2}{b'^2} - 1\right)$$
$$= \frac{2\mu}{a}\left(\frac{2a^2 - (a^2\sin^2\phi + b^2\cos^2\phi)}{a^2\sin^2\phi + b^2\cos^2\phi}\right)$$

Hence, putting c^2 for $a^2 - b^2$,

$$\sqrt{\frac{2\mu}{a}}\,dt = \frac{a^2\sin^2\phi + b^2\cos^2\phi}{\sqrt{a^2 + c^2\cos^2\phi}}\,d\phi,$$

or
$$\sqrt{\frac{2\mu}{a}}\,dt = a\,(1 - e^2\cos^2\phi)\,(1 + e^2\cos^2\phi)^{-\frac{1}{2}}\,d\phi.$$

Hence, by integration,

$$T\sqrt{\frac{2\mu}{a^3}} = \int_0^{2\pi} d\phi \sum_{n=0} e^{2n}\cos^{2n}\phi\,[C_n - C_{n-1}],$$

when
$$C_n = (-)^n\,\frac{1\,.\,3\,.\,5\,\ldots\,2n-1}{2\,.\,4\,.\,6\,\ldots\,2n}.$$

Thus, since
$$\int_0^{\pi/2}\cos^{2n}\phi\,d\phi = \frac{\pi}{2}\,C_n,$$

we have
$$T\sqrt{\frac{2\mu}{a^3}} = (-)^n\,\Sigma e^{2n}\,2\pi C_n^2\left(1 + \frac{2n}{2n-1}\right)$$
$$= 2\pi\left[1 - \frac{3}{1}\left(\frac{1}{2}\right)^2 e^2 + \frac{7}{3}\left(\frac{1\,.\,3}{2\,.\,4}\right)^2 e^4 - \frac{11}{5}\left(\frac{1\,.\,3\,.\,5}{2\,.\,4\,.\,6}\right)^2 e^6 + \text{etc.}\right]$$

The series on the right is convergent and, when the eccentricity is given, can be evaluated numerically (for example, when $e = \frac{2}{3}$, the series $= 1{\cdot}4342\,\pi$).

Thus we have the important result that the periodic time, as in simple elliptic orbits round *one* nucleus, is proportional to the

three-halves power of the length of the major axis of the ellipse, that is, $T = ka^{3/2}$, and when the eccentricity is practically prescribed by the auxochrome, the periodic time is proportional to $c^{3/2}$, since $c = ae$.

Explanation of the Colour Factors.

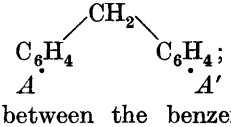
In the paper quoted, the linkage-factors for methylene-, imino-, oxo-, and thio-groups were given as respectively 0·65, 0·78, 0·891, and 0·92.

Now according to the present mathematical theory these four figures must be in the ratio of the four periodic times of revolution in the four different ellipses associated with the four prototype coloured substances [for example, dihydroxybenzhydrol, dihydroxydiphenylhydroxylamine (indophenol), and the corresponding peroxides and sulphoxides].

Therefore, from the foregoing theory we can find the ratio of the sizes of the ellipses (the ratios between their major axes) by extracting the two-thirds root of the four colour factors. The results are respectively 0·750, 0·847, 0·926, and 0·946.

The value unity now belongs to the imaginary major axis of an orbit going round two phenoxide-rings side by side, to which the vibration λ 1380 was assigned in the first paper of this series. To eliminate this imaginary factor we multiply the above four figures by (1 ÷ 0·926), thus making the oxygen compound the standard one.

The sizes of the four ellipses are then 0·810, 0·915, 1·000, and 1·021.

I now suggest a simple physical explanation of these figures, namely (1) that in the oxo-compound the molecule is in one straight line ($A{\cdot}C_6H_4{-}O{-}C_6H_4{\cdot}A'$); (2) that in the methylene compound the two halves of the molecule lie at the angle governed by the carbon tetrahedron (109·4°)  ; (3) that in the imino-compound the angle between the benzene rings is 133° when the compound is exhibiting its chief absorption band, and is (probably) 120° and 107° for subsidiary bands.

The distance between A and A' in the methylene compound is related to the distance between A and A' in the oxo-compound by a ratio which is the sine of half the angle of deviation, assuming that the carbon atom is only very slightly different in size from the oxygen atom. Now the sine of 109·4°/2 is just greater than the figure 0·81 found above for the methylene compound. If the oxygen atom is about 5 per cent. wider than the methylene–carbon

atom, the ratio of the distances AA' in the two cases is exactly 0·81, using the tetrahedral angle of 109·4°.

This being established, we can employ the colour data to find the hitherto unknown angle between the valencies of tervalent nitrogen. The fraction 0·915 is the sine of half the required angle, which is 132°. This becomes 133° if we assume the nitrogen atom to be intermediate in diameter between carbon and oxygen. This result is quite different from the angle assumed in the Hantzsch-Werner hypothesis (109°) and is also larger than the angle (120°) resulting from three equal plane valencies; but I do not think there is any evidence against the conception of three *unequal plane* valencies, the different combinations of which would explain the isomerism of the oximes, and would not involve the very definite asymmetry in the compounds Nabc which the Hantzsch-Werner hypothesis requires.

Now most of the phenazines, phenoxazines, and phenthiazines exhibit two bands at once in their spectrum. If this really connotes two simultaneous or alternative orbits, we can employ the measurements of the subsidiary bands to calculate the other angle (or angles) between the valencies of nitrogen. The imino-linkage colour-factor for this lower band is about 0·72 (that of the main band being 0·78). The two-thirds root of 0·72 is 0·80, and $0{\cdot}80 \div 0{\cdot}926 = 0{\cdot}86$. This is therefore the sine of half the required angle, which is 120° when corrected for the size of the nitrogen atom compared with oxygen.

We thus obtain 133° and 120° as the angles between two pairs of valencies in tervalent nitrogen. If the valencies are plane, the remaining angle is 360°—253° or 107°. If they are not plane, the third angle is smaller than this.

As regards the thio-compounds, of size 1·021, I suggest that they are straight like the oxo-compounds, and that the 2·1 per cent. difference is merely due to the larger diameter of the sulphur atom, which is known to have two octets of electrons instead of the one possessed by carbon, nitrogen, and oxygen.

Summary.

(*a*) The oxo-colour-factor 0·891 is $\left(0{\cdot}926 \sin \frac{180°}{2}\right)^{3/2}$.

(*b*) The two imino-factors, 0·78 and 0·72, are respectively $\left(0{\cdot}926 \sin \frac{133°}{2}\right)^{3/2}$ and $\left(0{\cdot}926 \sin \frac{120°}{2}\right)^{3/2}$, with a small correction for the smaller size of the nitrogen atom.

(*c*) The methylene-factor 0·65 is $\left(0{\cdot}926 \sin \frac{109{\cdot}4°}{2}\right)^{3/2}$ with an analogous small correction.

(*d*) The factor 0·926 is apparently the ratio of the size of the molecule of dihydroxydiphenyl oxide to the size of two juxtaposed molecules of phenol (both substances supposed ionised) and represents the contraction on replacing two para-hydrogen atoms by the oxo-linking.

GOVERNMENT LABORATORY,
HOSPITAL STREET, JOHANNESBURG. [*Received, May 16th*, 1922.]